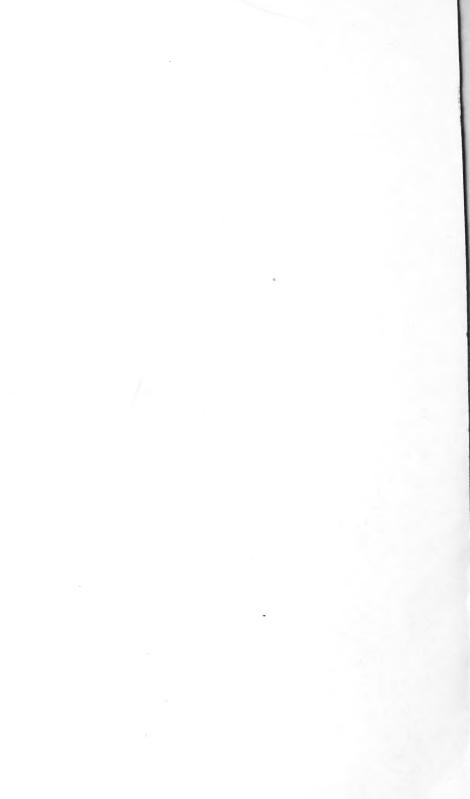
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# THE UTILIZATION OF CHERRY BY-PRODUCTS.

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#### INTRODUCTION.

The rapid development of the fruit-packing industry in the United States within recent years has had a tendency to direct the attention of packers to the large accumulations of by-products which at present are valueless because of their lack of utilization. The nature of these waste products differs, according to the fruit from which they result. In most cases some portion of the fruit is discarded because it has no further use. Often it is the exterior portion, but in many cases, especially with fruits which require pitting, the waste products consist of pits or seeds which must be removed before canning.

In previous publications of the Department of Agriculture<sup>1</sup> attention has been called to the enormous quantities of raisin seeds and peach and apricot pits which may be made to yield valuable commercial products, and already some manufacturers are turning their attention to these waste products with a view to their profitable utilization.

More recently the attention of the writer has been called by fruit packers to the waste which results from the cherry-packing industry of the North Atlantic, North-Central, and Western States. This is

<sup>&</sup>lt;sup>1</sup> Rabak, Frank. Peach, apricot, and prune kernels as by-products of the fruit industry of the United States. U. S. Dept. Agr., Bur. Plant Indus. Bul. 133, 34 p., 1908.

The utilization of waste raisin seeds. U. S. Dept. Agr., Bur. Plant Indus. Bul. 276, 36 p., 3 fig., 1913.

<sup>19348°-</sup>Bull. 350-16-1

material which has not only been discarded as valueless, but has actually been a source of expense, due to charges for hauling it away.

New York, Michigan, Wisconsin, and California produce the bulk of the cherries grown for canning purposes, and in preparing the fruit for canning large quantities of pits and juice accumulate.

# RELATION OF THE CHERRY TO SWEET AND BITTER ALMONDS AND ALLIED PLANTS.

The cherry belongs to the natural order Drupaceæ, which includes a number of our most important fruits, such as peaches, apricots, and prunes. It is a native of Asia Minor and has been introduced into Europe and the United States.

The fruit of the red sour cherry furnished the material for the following investigation, since it is mostly the fruit of this variety which is pitted for commercial use. The red sour cherry is designated botanically as *Prunus cerasus* L. Among the principal varieties grown commercially are the Montmorency Ordinaire, the Richmond, and the English Morello, the first named being the most important variety and producing the bulk of the fruit grown.

The peach, known botanically as Amygdalus persica L., the apricot, Amygdalus armeniaca L., and the prune, Prunus domestica L., are closely related to the cherry, as are also the sweet almond, Amygdalus communis dulcis DC. and the bitter almond, Amygdalus communis amara DC. All of these species, including the cherry, produce drupaceous fruits which, although of somewhat different sizes and shapes, possess the same general characteristics.

The kernels of both the sweet and bitter almonds yield products of commercial value, as do also the kernels of the peach, apricot, and prune. From the standpoint of chemical composition the kernels of these various species, and also of the cherry, are for the most part identical. All consist principally of a fatty oil and protein, with smaller quantities of sugar, mucilage, and the glucosid amygdalin.

It is generally known that bitter almonds yield two important commercial products, namely, fixed oil and volatile oil. The fixed oil is obtained from the kernels by expression, while the volatile oil is the result of a chemical process induced by the action of the enzym emulsin upon the glucosid amygdalin. It has been found that peach, apricot, and prune kernels also yield oils very similar to those obtained from bitter almonds.<sup>1</sup> The present investigation has shown that cherry kernels likewise are capable of yielding similar oils.

#### COMMERCIAL IMPORTANCE OF CHERRIES.

As has been stated, the pitting and canning of cherries is restricted almost entirely to the red sour cherries. A variety of sweet cherry,

the Napoleon (syn., Royal Ann), is cultivated extensively in California, and to a lesser degree in Oregon and Washington. This is used partly to supply the demand for the bottled cherries of commerce known as the maraschino cherries. Most of the cherries used for this purpose, however, are imported from Spain and Italy. These are pitted and bottled in the United States and constitute an important article of commerce. A large accumulation of pits results from the packing of the imported cherries, and the present investigation has been extended to include this waste product, as well as the waste resulting from domestic cherries.

The extent of the cherry-packing industry is indicated in the agricultural statistics of the States mentioned. According to the Thirteenth Census of the United States, the quantity of cherries grown in New York in 1909 was 271,597 bushels, in Michigan 338,945 bushels, and in Wisconsin 81,340 bushels, making a total of 691,882 bushels, or 20,756 tons. The quantity grown at the present time is doubtless considerably in excess of these figures. Approximately 80 per cent of the crop is canned, which is equivalent to 553,506 bushels, or 16,605 tons. The total output of the California orchards in 1909 was 501,013 bushels, or about 15,000 tons.

Accurate figures showing the total quantity of cherries pitted annually are not available. Approximate figures, however, were obtained by correspondence and by consultation with the principal packers in the various canning sections. The average annual importation of maraschino cherries from Italy and Spain, as calculated from the quantity of pits which result, is about 2,500 tons.

# ACCUMULATION AND DISPOSAL OF BY-PRODUCTS.

Two by-products of the cherry industry, the pits and the juice, are at present entirely wasted. From the standpoint of commercial utilization the pits constitute the larger and more important of these waste products.

It has been estimated that about 15 per cent of the cherries consists of pits. Since definite information regarding the total quantity of cherries pitted was unavailable and since the quantity pitted is dependent entirely upon the crop of each season, only approximate figures regarding the total output of waste pits are presented.

The figures given were obtained by interviews and correspondence with 23 packers in New York, 6 in Michigan, and 3 in California, who estimated the quantity of waste pits in 1914 as follows: New York, 800 tons; Michigan, 200 tons; and California, 400 tons. The total output was probably somewhat greater, as several packers failed to supply estimates. Wisconsin is rapidly increasing the acreage of cherries and, as predicted by growers, will probably produce several

hundred tons annually. Smaller quantities are also available in New Jersey and Pennsylvania.

From the figures given by the packers it would appear that 1,600 tons is a conservative estimate for the total quantity of cherry pits that become available each year. This quantity will most likely increase, owing to the increasing acreage.

The cherry juice which results from this industry accumulates in very large quantities. According to one prominent packer the quantity of juice is estimated at about 70 gallons per ton of cherries. Calculated on the quantity of cherries pitted, it is estimated that the approximate output of juice is 112,000 gallons annually. At the present time this by-product is entirely wasted, although several packers have attempted to find some use for it.

The pits of the imported cherries have also been discarded, and often at considerable expense. About 650 tons may be considered as the annual output of this waste.

The writer was informed by nearly all the packers consulted that much thought has been given to a possible utilization of the large quantities of waste material and that great benefit would result and an added stimulus be given to this important branch of the fruit industry if a profitable utilization of the waste products could be accomplished.

Actuated, therefore, by the requests of many packers and by actual observation of the large quantities of pits and juice which accumulate at the packing plants, the investigation herein described was undertaken.

# COMMERCIAL PRODUCTS OBTAINABLE FROM CHERRY PITS.

Because of the relationship of the cherry to the sweet and bitter almonds and to the peach, apricot, and prune, it was not unreasonable to suppose that products could be obtained from the pits of the cherry similar to those obtained from the other fruits mentioned. Fixed and volatile oils are at present manufactured from almonds and from peach and apricot kernels. The oils from these various kernels are practically identical in character and may be used for similar purposes; in fact, they are so nearly alike that much of the almond oil of commerce has been obtained from peach and apricot kernels. The composition of the kernels from cherry pits is such as to admit of the extraction of fixed and volatile oils, both possessing the general characteristics of almond oils.

The pits of the imported cherries present a somewhat different problem, due to the treatment of the fruit before importation. At the time these cherries are picked the kernels contain presumably the same constituents as the domestic cherries. The composition is notably altered, however, by the processes involved in packing. Briefly, the fruit receives the following treatment: When ripe it is picked and placed in trays, and then subjected to the bleaching action of sulphur dioxid, which changes the red color of the fruit to a pale yellow. After bleaching, it is packed in a 3 per cent salt brine in casks having a capacity of 350 pounds, in which containers it is imported, the cherries remaining in the brine for about four months.

In bottling the cherries the first step consists in washing them with successive portions of fresh water until all the salt is removed. The cherries are then pitted by hand, women being employed for this operation. After pitting, the fruit is packed in the bottles by hand, and hot sirup is poured over it, together with an artificial red coloring matter and a small quantity of bitter-almond oil, the latter being added to impart the cherry flavor.

Upon examining the kernels of the pits which were removed from these cherries before bottling, it was observed that when the kernels were crushed in the mouth no volatile oil was apparent. It is quite probable that the action of the sulphur dioxid and the salt brine exerts a detrimental influence upon the glucosid contained in the kernel. The fact that no bitter-almond taste developed was conclusive evidence that the amygdalin had been destroyed or its hydrolysis impaired by the treatment the fruit had received. However, a fixed oil was found to be present in the kernels and its quality was not seriously impaired, as will be shown later.

The juice from the domestic cherries is extremely acid in taste, but after neutralization of the acid considerable sugar was noted. The preparation of alcohol from the waste juice and the possibility of reducing the juice to a sirup were considered. It was thought probable also that by means of some jelling medium the juice might be used

for making jelly.

Attention may also be directed to the meal which results after the extraction of the fixed and volatile oils from the pits and kernels. This meal is rich in nutritive constituents and should find a useful outlet in commerce.

Briefly summarizing: A number of products may be obtained from the pits and kernels of cherries and from the juice, which, as will be shown, may prove of commercial importance.

#### FIXED OIL.

#### METHODS OF EXTRACTION.

The extraction of a fixed oil from seeds is usually accomplished by one of two methods: The use of hydraulic pressure or of volatile solvents. Both methods have a general application.

Volatile solvents are used in many instances, especially in the case of seeds which are more or less deficient in oil. In all cases the sol-

vents used are such as will readily dissolve the oil. Among those employed are gasoline, ether, benzene, petroleum ether, chloroform, carbon bisulphid, and carbon tetrachlorid. Apparatus of the continuous-extraction type is usually employed. This admits of the recovery of the solvent and minimizes the loss of the solvent. It has been reported that recent improvements in method and apparatus have made this process cheaper than the pressure method. The solvent can be entirely removed from both the oil and the residue. It is also held that by the employment of this process various kinds of material can be treated in the same apparatus. The expense of operating is also said to be less than the pressure method.

The color of oils extracted by solvents is often very dark and it is necessary to remove it, but this can usually be accomplished with no great difficulty.

The solvents perhaps most frequently employed, because of their comparatively low price, are benzene, petroleum ether, gasoline, and carbon tetrachlorid. Of these, carbon tetrachlorid has within recent years become very popular, not only because of its cheapness but because of its noninflammability and less volatile nature, thus reducing the danger from fire and minimizing the loss from evaporation. According to a recent report benzine is used for the extraction of soy-bean oil in a new mill of the South Manchurian Railway Co. at Dairen, this mill having a capacity of 80 tons daily.

Hydraulic pressure is perhaps more universally used than any other method and especially in the case of seeds having a high percentage of oil. This method is not practicable, however, with seeds of low oil content, because the resulting press cake retains a considerble percentage of the oil, and this would materially affect the total yield. Seeds which contain as high as 30 to 50 per cent of oil are best manipulated by extraction under pressure from hot meal or with heated plates, a maximum percentage of oil being thereby obtained. As a general rule, the quality of an oil obtained by hydraulic pressure excels that obtained by volatile solvents, cold pressure producing even better quality than hot pressure. Oils obtained by the pressure method invariably contain less impurities than those extracted by solvents, and therefore require less refining.

Suitable presses for extracting fixed oils are on the market, all embodying the same general principle. Continuous extractors, preferably of copper, are also obtainable from American manufacturers, especially manufacturers of pharmaceutical machinery.

EXTRACTION OF OIL FROM THE PITS BY SOLVENTS.

A quantity of dry pits was finely ground in a drug mill and introduced into a continuous-extraction apparatus fashioned after the

<sup>&</sup>lt;sup>1</sup> Parlett, H. G. New bean-oil extracting mill at Dairen on the benzine system. *In* Bd. Trade Jour. [London], v. 86, no. 923, p. 385, 1914.

Soxhlet extractor. Extraction was made with ether and continued until the material was completely exhausted. By this process a yield of 8.3 per cent of a pale-brown fixed oil was obtained. By the same process the pits from the imported cherries yielded 4.5 per cent of a deep-brown, rancid-smelling oil.

The crude oil thus obtained was not only deeply colored but possessed a characteristic odor of rancidity, due to the presence of free volatile fatty acids. In order to free the oil of the objectionable color and odor it was subjected to the following refining process: The oil was introduced into a flask and live steam was conducted through the mass until the distillate which contained the free volatile acids possessed no appreciable odor and was no longer acid to litmus. While hot, the oil was separated from the water in the flask by means of a separatory funnel, treated with kaolin (fuller's earth), and the mass filtered through filter paper in a hot filtration funnel. The filtered oil was pale golden yellow in color, with a distinctly nutlike taste and with no suggestion of rancidity.

#### EXTRACTION OF OIL FROM THE KERNELS BY PRESSURE.

Hydraulic pressure was not found applicable to the pits, because of the low yield of oil. It was necessary, therefore, to crack the pits and remove the kernels. This was accomplished by slowly feeding the pits into a mill having vertical grinding plates set to grind very coarsely, so that a mere cracking of the shells resulted without crushing the kernels. The cracked pits were first put through a roundhole sieve with openings sixteen sixty-fourths of an inch in diameter and then through another sieve with openings of thirteen sixty-fourths of an inch. This removed the coarser parts of the shells. A final separation was made by passing the material through a "wildoat" sieve with oblong meshes measuring seven sixty-fourths by one-half of an inch. The last screening effected a reasonably complete separation of the kernels from the shells.

It is very important that the mill be fed with a slow, continuous stream of pits, and care must be exercised in order not to crush the kernels, otherwise they are apt to separate into halves and the halves pass through the final sieve. By this process 28 per cent of the pits was found to consist of kernels.

The laboratory press available for the extraction of the oil from the kernels was not entirely adequate for obtaining the best results. A pressure of 2,750 pounds to the square inch was applied to the finely ground kernels, the expression being conducted in the cold. A yield of 21 per cent of a pale golden yellow oil, with a pleasant nutlike odor and taste, was thus obtained. With a commercial hydraulic press of the latest type, equipped for hot expression, a much higher yield would undoubtedly result. Working on a commercial scale

with an efficient hydraulic press or oil expeller, a yield of at least 30 per cent of oil should be obtained.

For the purpose of comparing the yield and general characteristics of the oils obtained from cherry kernels by solvent and by expression with oils from related kernels, Table I was compiled.

Table I.—Yield and physical properties of crude and refined cherry oils compared with other related oils.

| Source of oil.   | Yield<br>of oil. | Spe-<br>cific<br>gravity<br>at 23°<br>C. | Index<br>of re-<br>fraction<br>at 23°<br>C. | Congealing point.   | Color.              | Odor.                                      | Taste.                                 |
|--|------------------|--|---|---|---------------------|--|--|
| Cherry pits (red<br>sour cherries):<br>Crude   |                  | 0.9204                                   | 1.4697                                      | Turbid at $-8^{\circ}$ C.; almost solid at $-12^{\circ}$ C. | Pale brown          | Slightly raneid                            | Slightly acid, fatty, slightly bitter. |
| Refined  |                  | .9171                                    | 1.4700                                      | Turbid at -8° C.; nearly solid at -15° C.                   | Pale golden yellow. | Bland, fatty                               | Bland, fatty, nutlike.                 |
| Cherry kernels<br>(red sour cher-<br>ries).<br>Cherry pits(im-<br>ported cher-<br>ries): | 132              | 2.9150                                   | 1.4727                                      | Turbid at -13° C.; semisolid at -18° C.                     | Pale golden         | Pleasant, nut-<br>like.                    | Bland, nutty, agreeable.               |
| Crude  |                  | . 9302                                   |   | Semisolid at<br>-11° C.<br>Semisolid at                     |                     | Fatty, slightly<br>rancid.<br>Bland, fatty | Fatty, slightly acid. Bland, fatty.    |
| Cherry kernels   | 1 50             | .9156                                    | 1.4775                                      | -16° C.   |                     |  | Fatty and nut-<br>like.                |
| cherries).<br>Peach kernels <sup>3</sup> .   | 39. 5            | 4.9166                                   |   | Solidifying<br>point below<br>-20° C.5                      | Yellowish           | Fatty, nearly odorless.                    | Bland, _ fatty, nutty.                 |
| Apricot ker-<br>nels. <sup>3</sup>   | 40               | 4.9168                                   | 61.4712                                     | 20° C.6   | Straw colored.      | Slightly fatty,<br>nearly odor-<br>less.   | Fatty and nut                          |
| Prune kernels <sup>3</sup> .   | 35               | 4.9164                                   |   | −10° C.7  | Golden yellow.      | Fatty, nutlike.                            | Bland, nutty<br>slightly<br>sweet.     |
| Sweet almonds<br>(Spain),3   | 49               |  |   | −21° C.8  |                     | less, fatty.                               | Nutlike and                            |
| Bitter almonds<br>(Italy).3  | 42.3             | 4.9158                                   | 91.4705                                     | −10° C.8  | Yellow              | do   | Bland and                              |

1 By ether extraction.

An examination of Table I shows that the specific gravity of the refined oil from the pits and of the expressed oil from the kernels corresponds very closely with that of the oils from the other kernels enumerated, thus indicating a like composition of all the oils, since the specific gravity of fixed oils is a property which is influenced largely by its composition. The high specific gravity of the crude pit oil is attributed to the presence of impurities, largely in the form of free fatty acids, which later were removed in the refining process.

Specific gravity and other physical constants represent expressed oil of cherry kernels.
 Rabak, Frank. Peach, apricot, and prune Fernels as by-products of the fruit industry of the United States. U. S. Dept. Agr., Bur. Plant Indus. Bul. 133, p. 15, 1908.
 At 25° C.

<sup>&</sup>lt;sup>5</sup> Lewkowitsch, J. Chemical Technology and Analysis of Oils, Fats, and Waxes, v. 2, p. 232. London, 1909.

<sup>999.

6</sup> At 20° C., see Lewkowitsch, J., op. cit., p. 228.

7 Lewkowitsch, J., op. cit., p. 230.

8 Lewkowitsch, J., op. cit., p. 235.

9 At 25° C., see Lewkowitsch, J., op. cit., p. 236.

The refractive index appears likewise to be affected by the presence of free fatty acids as impurities. The crude oils are seen to possess a lower refractive index than those which have been refined and which therefore contain less impurities. The refractive property of the refined oils corresponds very closely with that of the other oils included in Table I.

The congealing point is a property which is affected by differences in composition. Oils of the same kind, whether crude or refined, often differ in the congealing point, as is shown by the oils from the pits of both the domestic and the imported cherries. The refined cherry oil compares favorably in this respect with the other oils tested.

No marked difference is observed in the color, odor, or taste of the various oils except that the crude oils are slightly darker and have a less agreeable odor and taste than the other oils.

For the purpose of making a further comparison it was deemed advisable to determine the so-called chemical constants (the acid, saponification, and iodin values), which are shown in Table II.

Table II.—Chemical constants of cherry oils compared with various other fruitkernel oils,

|                           | Free fatty acids. |  | Sa-                              |                 |                                       | Free<br>aci    | fatty<br>ds.                                 | Sa-                              |                 |
|---------------------------|-------------------|--|----------------------------------|-----------------|---------------------------------------|----------------|--|----------------------------------|-----------------|
| Source of oil             | Acid<br>value.    | Cal-<br>cu-<br>lated<br>as<br>oleic<br>acid. | poni-<br>fica-<br>tion<br>value. | Iodin<br>value. | Source of oil.                        | Acid<br>value. | Cal-<br>cu-<br>lated<br>as<br>oleic<br>acid. | poni-<br>fica-<br>tion<br>value. | Iodin<br>value, |
|                           |                   |  |                                  |                 |                                       |                |  |                                  |                 |
| Cherry pits (red sour     |                   | D et   |                                  |                 | Cherry kernels (import-               | 0 ~            | P.ct.  |                                  |                 |
| cherries):<br>Crude       | 21.5              | P.ct.<br>10.90                               | 189. 2                           | 101.7           | ed cherries)<br>Peach kernels 3       | 3, 5           | 1.76<br>.41                                  | 188. 5<br>187                    | 108. 2<br>110   |
| Refined                   | 1 5. 1            |  | 186. 4                           | 102. 4          | Apricot kernels 3                     | .75            | .38  | 203                              | 107             |
| Cherry kernels (red sour  |                   |  |                                  |                 | Apricot kernels (same as              |                |  |                                  |                 |
| cherries) cold pressed 2. | 6.2               | 3.13   | 187.6                            | 106.9           | above, 1 year old)<br>Prune kernels 3 | 13.3           |  | 180                              | 118             |
| Cherry pits (imported     |                   |  |                                  |                 | Prune kernels 3                       | 1.9            | .95  | 160                              | 105             |
| cherries):<br>Crude       | 22. 1             | 11.10  | 185 2                            | 110.3           | Sweet almonds (market sample) 3       | 3, 5           | 1.76   | 193                              | 107.3           |
| Refined                   | 1 8. 4            | 4. 10  | 189.8                            | 111.4           | Bitter almonds 3                      |                | .86  | 188                              | 106.3           |
|                           |                   |  |                                  |                 |                                       |                |  |                                  |                 |

<sup>&</sup>lt;sup>1</sup> Acid number determined after standing 6 months.

Before discussing the data in Table II it should be mentioned that the amount of free fatty acids in an oil is wholly dependent upon the age of the oil or of the material from which it is extracted. Freshly expressed or extracted oils from fresh material show but a trace of free acids, often less than 1 per cent. Most fatty oils are unstable as regards the liberation of free fatty acids, the quantity increasing with the age of the oil.

The crude oils from the cherry pits show a high acid content, which, however, was largely reduced in the process of refining. The

<sup>&</sup>lt;sup>2</sup> Kernels obtained from pits about 1 year old.
<sup>3</sup> Rabak, Frank. Peach, apricot, and prume kernels as by-products of the fruit industry of the United States. U. S. Dept. Agr., Bur. Plant Indus. Bul. 133, p. 16, 1908.

cold-pressed oil from the kernels of the domestic cherries, although examined immediately after extraction, contained considerable free acidity. This was doubtless due to the fact that the kernels were taken from pits which had been kept in the laboratory for about a year. As a general rule, oil from old seeds is high in acid content.

The acidity of the oil from the kernels of the imported cherries was considerably lower, due possibly to freshness of the kernels.

With two exceptions, the related oils included in Table II are low in acidity, due to the fresh condition of the oil when examined. Of the two exceptions, one of the oils was a year old before the determination of the free acidity was made, and the other was a market sample, the age of which was not known.

The saponification and iodin values of the cherry oils, which values are a criterion of the composition, agree quite closely with each other and compare favorably with the other oils, only an occasional variation occurring.

From the standpoint of general chemical composition, therefore, the refined oil from the cherry pits and the expressed oil from the kernels are very similar to almond oils and to the oils from peach, apricot, and prune kernels.

# CHEMICAL EXAMINATION OF THE FIXED OIL.

The general nature of the fixed oil having been determined, a more detailed analysis was made in order to obtain information bearing on the composition of the oil and to note the effect of refining on the more important properties.

Besides the acid, saponification, and iodin values, the following additional constants were determined, according to the method recommended by the Association of Official Agricultural Chemists:

The *volatile acids*, consisting of the glycerids of such acids as butyric, valerianic, caproic, etc., were determined and expressed as the Reichert-Meissl number, which is a measure of the volatile acids expressed in cubic centimeters of decinormal alkali required to neutralize the volatile acids contained in 5 grams of oil.<sup>2</sup>

The soluble and insoluble acids were determined, the former representing the percentage of soluble acids calculated as butyric acid and the latter the percentage of insoluble fatty acids (Hehner value).<sup>3</sup>

The acetyl value, which is a measure of the glycerids of hydroxy fatty acids, was determined largely for comparative purposes.<sup>4</sup>

Likewise the *unsaponifiable matter*, which is a variable characteristic, was determined.<sup>5</sup> The percentage of unsaponifiable matter in a fixed oil is regulated largely by the presence of variable quantities of an alcoholic substance, phytosterol, and other substances, such as coloring matter and waxlike compounds.

<sup>&</sup>lt;sup>1</sup> Wiley, H. W., ed. Official and provisional methods of analysis, Association of Official Agricultural Chemists. As compiled by the committee on revision of methods. U. S. Dept. Agr., Bur. Chem. Bul. 107 (rev.), 272 p., 13 fig., 1908.

<sup>&</sup>lt;sup>2</sup> Wiley, H. W., op. cit., p. 139.

<sup>&</sup>lt;sup>3</sup> Wiley, H. W., op. cit., p. 138, 139.

<sup>\*</sup> Wiley, H. W., op. cit., p. 142.

<sup>&</sup>lt;sup>5</sup> Wiley, H. W., op. cit., p. 144.

The insoluble acids comprise the largest portion of all fixed oils, and these were studied in detail by resolving them into the solid and liquid acids of which they are composed. The nature of the solid and liquid acids of an oil is of importance, since upon the percentage of these respective acids depends largely the application of the oil in commerce, whether it can be used for edible purposes, for soap making, or as a drying oil.

The separation of the solid and liquid acids was accomplished by the lead-ether method.<sup>1</sup> The efficacy of this method depends upon the solubility in cold ether of the lead salts of the liquid acids and the insolubility of the same salts of the solid acids. After the separation of the solid and liquid acids the physical and chemical properties of each were determined, from which the approximate composition of the oils was deduced.

The foregoing methods were applied to the crude oil which was extracted from the pits of the domestic cherries by ether; also to the refined oil from the pits and to the expressed oil from the kernels. The results of these determinations are given in Table III.

Table III.—Chemical characteristics of the oils from cherry pits and kernels.

| Source of oil.  | Volatile<br>acid, or<br>Reichert-<br>Meissl<br>number. | Soluble<br>acids (cal-<br>culated as<br>butyric<br>acid), | Insoluble acids.                | Acetyl<br>value.      | Unsaponi-<br>fiable.    |
|---|--|---|---------------------------------|-----------------------|-------------------------|
| Cherry pits (red sour cherries); Crude Refined Cherry kernels (red sour cherries) | Per cent. 6.32 3.665 4.72                              | Per cent.<br>1,22<br>,473<br>,469                         | Per cent.<br>92<br>92.5<br>92.8 | 20.3<br>3.45<br>12.67 | Per cent. 2.45 1.12 .44 |

The data in Table III clearly show the effect of the refining process upon the composition of the oils. The refined oil from the pits more nearly approaches the expressed oil from the kernels. As would be expected, the content of volatile acids is highest in the crude oil from the pits, while the refined oil differs only slightly in this respect from the kernel oil.

The percentage of soluble acids, calculated as butyric acid, decreases much the same as the volatile acids. The crude pit oil shows 1.22 per cent of butyric acid, which in the refined oil is reduced to 0.473 per cent. The refined oil nearly corresponds with the kernel oil.

The insoluble acids, which constitute by far the greatest portion of the oil, show only slight differences in the three oils.

The acetyl values given represent the true values after correction for the volatile acids. If indicated without correction they would be too high by the amount of volatile acids present. Here, also, is

<sup>&</sup>lt;sup>1</sup> Wiley, H. W., op. cit., p. 142, 145.

seen the favorable effect of the refining process. The acetyl value of 20.3 in the crude pit oil was reduced to 3.45 in the refined oil. The kernel oil, however, shows a considerably higher acetyl value than the refined oil from the pits. This is due to the fact that the kernels were taken from pits which were not in fresh condition.

The amount of unsaponifiable matter in an oil depends largely upon the amount of coloring matter and waxlike substances contained in it. Therefore, the crude oil would be expected to show the highest percentage, which is substantiated by the results obtained.

As previously stated, the insoluble acids are most important factors in determining the quality and usefulness of an oil. Therefore, the physical and chemical constants of these acids were determined, and the results are presented in Table IV. For the purpose of comparison, the known constants of a number of related oils are also included in Table IV.

Table IV .- Physical and chemical constants of insoluble acids of oils from cherry pits and kernels and from other fruit kernels.

| Source of oil.                     | Color.     | Odor.                        | Ta <b>s</b> te.             | Spe-<br>cific<br>gravity<br>at 25°C. | Refrac-<br>tive<br>index<br>at 25°C. | Congeal-<br>ing point.   | Neu-<br>trali-<br>zation<br>value. | Iod'n<br>value.           |
|------------------------------------|------------|------------------------------|-----------------------------|--------------------------------------|--------------------------------------|--------------------------|------------------------------------|---------------------------|
| Cherry pits:                       |            | , ,                          | bitter.                     | 0.9019                               | 1.4635                               | ° C.<br>12 to 11         | 192.4                              | 99.9                      |
| Cherry ker-                        | Pole straw | cid, fatty. Nutlike, slight- | Sweetish, fatty,<br>bitter. |                                      | 1.4641<br>1.4635                     | 12.5 to 12<br>13.5 to 13 | 179.7<br>180.8                     | 93.7<br>92.8              |
| nels.                              |            | ly rancid.                   | slightly bit-<br>ter.       |                                      |                                      |                          |                                    |                           |
| Peach ker-<br>nels. <sup>1</sup>   |            | •••••                        |                             |                                      |                                      | 13.5 to 13               | 205<br>to<br>209, 9                | 94. 1<br>to<br>101. 9     |
| Apricot ker-<br>nels. <sup>2</sup> |            |                              |                             | . 9195                               |                                      |                          | 194                                | 99. 4<br>to<br>103. 8     |
| Prune ker-<br>nels.3               |            |                              |                             |                                      |                                      | 13 to 12                 | 200.4                              | 95.7<br>to                |
| Almond ker-<br>nels.4              |            |                              | ,                           |                                      | 1. 4461                              | 11.8<br>to<br>11.3       | 204                                | 102<br>93.5<br>to<br>96.5 |

<sup>&</sup>lt;sup>1</sup> Lewkowitsch, J. Chemical Technology and Analysis of Oils, Fats, and Waxes, vol. 2, p. 232. London, 1909.

Only slight differences in the physical properties—color, odor, and taste—of the insoluble acids are noted in the cherry oils. Data on these points were not available for the other oils. The specific gravity, refractive index, and congealing points of the insoluble acids of cherry oils compare favorably with the same constants of the related The neutralization values differ somewhat from those of the related oils, with the exception of the crude pit oil. This indicates a slightly different composition from the standpoint of fatty acids. The iodin value, which indicates the content of unsaturated acids,

<sup>&</sup>lt;sup>2</sup> Specific gravity at 15° C., see Lewkowitsch, J., op. cit., p. 228.
<sup>3</sup> Lewkowitsch, J., op. cit., p. 230.
<sup>4</sup> Refractive index at 60° C., see Lewkowitsch, J., op. cit., p. 237.

compares favorably with the related oils. General factors, such as the age of the oil and the time intervening between the separation of the insoluble acids and the determination of the constants, would tend to modify the results obtained.

For the purpose of comparison, the physical and chemical characteristics of the solid and liquid acids, after separation from the insoluble acids, were determined, and the results are given in Table V.

Table V.—Physical and chemical constants of solid and liquid acids of oils from cherry pits and kernels.

|                             | Solid acids.          |   |  |        | Liquid acids.      |  |        |  |                                    |                 |  |  |
|-----------------------------|-----------------------|---|--|--------|--------------------|--|--------|--|------------------------------------|-----------------|--|--|
| Source<br>of oil.<br>Yield. |                       | Description.                                      | m. Melt-<br>ing<br>point. Neu-<br>traliza-<br>tion<br>value. |        | Yield.             | eld. Description.  |        | Re-<br>fractive<br>index<br>at<br>25° C. | Neu-<br>traliza-<br>tion<br>value. | Iodin<br>value. |  |  |
| Cherry<br>pits:<br>Crude    | Per<br>cent.<br>6. 27 | White, waxy mass, fatty odor.                     | ° C.<br>51   | 197. 2 | Per<br>cent.<br>84 | Golden - yellow<br>liquid, with<br>nutlike odor,<br>and sweet,                           | 0.8917 | 1. 4603                                  | 185.1                              | 98              |  |  |
| Refined.                    | 8, 94                 | White, waxy mass, with tallowlike taste.          | 49.0   | 192.3  | 83.2               | fatty taste.  Brownish oil, liquid, with nutlike odor, and sweet and bitter after taste. | . 9028 | 1. 4643                                  | 188. 2                             | 108.7           |  |  |
| Cherry kernels.             | 8.96                  | White, waxy mass, with fatty odor, tallowy taste. | 49.5   | 205. 1 | 82.8               | Straw colored,<br>with slightly<br>rancid odor<br>and sweetish<br>bitter taste.          | . 8941 | 1. 4617                                  | 190.6                              | 114             |  |  |

From Table V it will be observed that the solid acids constitute only a small portion of the cherry oils. The crude oil from the pits shows a considerably lower percentage than either the refined oil or the kernel oil. The general physical properties are practically the same. No marked differences are noted in the melting points or in the neutralization value. Judging from the neutralization values it is very probable that the major part of the solid acids consists of stearic acid, which theoretically has a neutralization value of 197.5. The melting point of pure stearic acid is 69° C., but the commercial article is often contaminated with other acids and has been known to melt as low as 56° C. The low melting point of the solid acids in the cherry oils may be attributed to impurities, as the determinations were made without any attempt at purification.

It may safely be assumed, therefore, that the solid acids of cherry oils consist chiefly of stearic acid, with possibly a slight admixture of palmitic acid, which has a neutralization value of 219 and a melting point of 62° C.

The liquid acids comprise the largest portion of the oils. The crude oil from the pits was found to contain 84 per cent, the refined oil 83.2

per cent, and the kernel oil 82.8 per cent. From the physical properties it is very probable that the bulk of the liquid acids consists of oleic acid. The specific gravity of pure oleic acid is reported as 0.895 at 25° C. and the index of refraction at the same temperature as 1.4603. These figures agree very closely with those recorded in Table V. The descriptions of the acids obtained are also very similar to the description of official oleic acid, which is described as yellowish or brownish yellow in color, with a peculiar lardlike odor and taste.

That the bulk of the liquid acids consists of oleic acid is further substantiated by the close agreement of the iodin value of these acids as found in the cherry oils and the iodin value of commercial oleic acid. Although the iodin value of the pure acid is 90, some oleic acids

of commerce have values as high as 100 to 110.

The somewhat low neutralization values found in the cherry oils are probably due to slight changes in the fatty acids, as it is well known that these are apt to decompose.

In approximating the composition of cherry oil, only the kernel oil was considered. It was found that this oil consisted of 8.96 per cent of solid acids, which were composed of stearic acid with a possible trace of palmitic acid. Since the glycerid stearin contains 95.73 per cent of stearic acid, it was found by calculation that the oil contained 9.36 per cent of stearin. The original oil consisted of 82.8 per cent of liquid acids, which, calculated as oleic acid and reduced to terms of olein (olein contains 95.7 per cent oleic acid), corresponds to 86.5 per cent of the glycerid olein.

A brief summary of the results obtained by the chemical examination indicates, therefore, the following approximate composition of cherry kernel oil: Olein, 86.5 per cent; stearin, including a possible trace of palmitin, 9.36 per cent; the remaining portion of the oil consists of smaller amounts of free acids, volatile acids, and unsaponifiable matter.

# REACTION OF THE OIL TOWARD REAGENTS.

Color reactions are frequently applied to fixed oils, although perhaps more for the purpose of detecting adulterations than for determining the quality. Certain reagents produce characteristic color reactions; therefore, when it is desired to compare related oils it is often expedient to ascertain the behavior of the oils toward reagents. Since this investigation deals with an oil which is closely related to several well-known commercial oils, a number of color reactions were therefore determined and comparison was made with the color reactions obtained from the affiliated oils extracted by means of ether in this laboratory. The results are presented in Table VI.

Table VI.—Color reactions of oils from cherry pits and kernels and of other related oils.

| (75 Elaidin test (fuming nitrio acid and water, equal parts).                             | Brown, dark Deep yellow solid mass brown. | to Deep yellow viscous mix-<br>ture, coorless liquid.             | sh ture, nearly color ess             | Д.                                  | Straw-colored solid with nearly colorless liquid. | Do.                      | Dark yellowish solid with nearly colorless                  | Pale yellow solid with colorless liquid.  Pale yellow solid with yellowish liquid. |
|---|---|---|---------------------------------------|-------------------------------------|---|--------------------------|---|--|
| Sulphuric acid (75<br>per cent).  | Brown, da                                 | Brownish red<br>brown.  | Pale brownish red<br>to greenish      | Brown to brown-ish red.             | Flesh   | Pale flesh               | with Deep pink  | Light pink   |
| Phloroglucin test (0.1 percent phloroglucin in ether applied in presence of mirric acid). | Reddish                                   | Dirty yellowish with Brownish with red Brownish red to pink tone. | Very pale pink color- Yellowish brown | Pale brownish with reddish border.  | Very pale pink                                    | Pale crimson             | Dark yellow with pinkish tinge.                             | doDeep crimson   |
| Bieber's test (equal parts furning ultric acid, sulphuric acid, and water).               | Dirty yellowish with Reddish              |   |                                       | Dark dirty yellow-                  | ×   | dodo.                    | Decided pink  | Very pale pink<br>Pale pink  |
| Nitric acid, fuming.  | Deep red-brown to<br>dark brown.          | Deep red to dark brownish red.                                    | Deep red to brown-ish red.            | Dark brownish red<br>to dark brown. | Light brownish red to brown.                      | Pale brownish red to     | Reddish to red-<br>brown.                                   | Light brownish red<br>to pale brown.<br>Pale trownish red to<br>pale brown.        |
| Nitric acid.  | Pale brown to dirty gray-brown.           | Reddish brown to dirty red.                                       | Pale pink to dirty lavender.          | Pale brownish                       | Very faintly pink to<br>dirty pink.               | ор                       | Peach kernels Very faint straw Pink to deep dirty lavender. | Pink to dirty lavender.  Deep pink to pale brownish red.                           |
| Original color.   | Golden yellow                             | Refined Deep straw  | Pale straw                            | Imported cherries. Deep straw       | Pale yellow                                       | Sweet almonds Pale straw | Very faint straw  | Apricot kernels Pale yellow Prune kernels Deep straw                               |
| Source of oil.  | Cherry pits:<br>Crude                     | Refined   | Cold pressed Pale straw               | Imported cherries.                  | Bitter almonds Pale yellow                        | Sweet almonds            | Peach kernels   | Apricot kernels Pale yellow Prune kernels Deep straw                               |

The color reactions obtained by the use of the various reagents show some differences, yet they bear a certain fixed relationship, differing usually only in intensity. From the color reactions produced it can not be stated that the quality of one oil is superior to that of any other, but a close relationship is clearly obvious. The test with fuming nitric acid and water, as prescribed in the United States Pharmacopæia<sup>1</sup> for the expressed almond oil, depends upon the formation of a polymerized solid compound with the olein of the oil. This test emphasized most strongly the similarity of cherry-kernel oil to official almond oil and also to the other related oils.

Inasmuch as almond kernels and peach and apricot kernels yield fixed oils of commercial value, attention is called to the close resemblance of cherry oil to these oils. Careful inspection of the chemical and physical properties has shown that, although it is not identical with either almond, peach, or apricot oil, it is not fundamentally different from any of these. The variations observed may not be due wholly to difference in composition, since often fixed oils from the same source possess varying properties. The condition of the material from which the oil is extracted and also the seasonal factors are influential in affecting the ultimate quality of an oil.

Because of this close relationship, cherry-kernel oil should therefore be adapted to the same uses for which the other oils are employed.

#### AVAILABLE QUANTITY OF THE FIXED OIL.

Of first importance in connection with the possible commercial utilization of waste cherry pits is the available quantity of the material. A conservative estimate of a normal year's output from the red sour cherries is 1,600 tons. By actual experiment it was found that 28 per cent of the pits consists of kernels. On this basis there would be available annually 448 tons of kernels. By the use of modern hydraulic presses this quantity of kernels should yield 134 tons of fixed oil, or 268,000 pounds. In addition to this, there is also an annual accumulation of about 650 tons of pits from the imported cherries. Only 9 per cent of these pits was found to consist of The quantity of kernels available from this source, therefore, would be 58.5 tons. On extraction with ether these kernels vielded 50 per cent of oil. Subjected to hydraulic pressure about 45 per cent would be obtainable, which would give approximately 26 tons, or 52,000 pounds of oil. Therefore, the total quantity of fixed oil available from the annual accumulation of cherry pits, both domestic and imported, would be 160 tons, or 320,000 pounds.

 $<sup>^{\</sup>rm i}$  The Pharmacopæia of the United States . . . Eighth decennial revision, p. 307. Philadelphia, 1907.

#### USES OF THE FIXED OIL.

Cherry oil should be adapted to all purposes for which almond, peach, or apricot oil is used. Almond oil is used chiefly in pharmaceutical preparations, and the demand is considerable. Therapeutically, peach and apricot oils are as efficient as almond oil. Peach and apricot oils have recently been manufactured in California for use as edible oils and are said to excel olive oil in flavor and taste.

#### VALUE OF THE FIXED OIL.

The value of cherry oil would naturally depend upon its use and the demand for oils of this character. The importation of sweet and bitter almond oil for the year ended June 30, 1914, was 38,586 pounds, valued at \$36,620.¹ The price of peach-kernel oil has ranged from 22 cents a pound in 1913 to 45 cents in 1915. No data are available regarding the extent of the importation of this oil or of apricot oil, although it is known that large quantities are imported annually.

#### VOLATILE OIL.

#### METHOD OF EXTRACTION.

The volatile oil does not exist as such in the kernels, but is the result of glucosidal hydrolysis, the glucosid amygdalin reacting with the ferment emulsin in the presence of water. It is one of the comparatively few oils which are obtained only after chemical reaction has taken place.

The first step necessary in extracting the volatile oil from the kernels was to produce the reaction between the glucosid amygdalin and the ferment emulsin under conditions which would insure a complete formation of the oil. This was best accomplished by the method formulated in a previous investigation, which in substance is as follows: To one part of the ground kernels or press cake add two or three parts of lukewarm water, and macerate with frequent agitation for about one hour, after which pass steam, under slight pressure, into the mixture and distill until approximately four parts of distillate are obtained. The volatile oil, which is heavier than water, will separate on the bottom of the receiving vessel. The upper aqueous distillate, which is saturated with the oil in solution, can be drawn off and subjected to distillation by the direct application of heat. This process can be continued until the full yield of oil is obtained.

<sup>&</sup>lt;sup>1</sup> U. S. Department of Commerce. Foreign Commerce and Navigation of the United States for the Year Ending June 30, 1914, pp. 820-821. Washington, 1915.

<sup>&</sup>lt;sup>2</sup> Rabak, Frank. Peach, apricot, and prune kernels as by-products of the fruit industry of the United States. U. S. Dept. Agr., Bur. Plant Indus, Bul. 133, p. 24, 1908.

In order to obtain the maximum yield it is very important that the maceration of the ground material be made with lukewarm water, as the reaction between the constituents, with the formation of oil, takes place most expeditiously at that temperature. It is also necessary to conduct the maceration in a closed vessel, preferably in the still itself, in order to avoid the loss of oil by evaporation.

As a preliminary experiment, a quantity of ground pits was treated according to this method and distilled in a still consisting essentially of a still body and a condenser. Live steam was passed into the macerated mixture, and the distillate collected in a receiving vessel of glass, from which the aqueous distillate was easily decanted. The oil accumulated on the bottom, and the final separation was made by means of a separatory funnel. After cohobation of the distillate, which consists in redistilling by direct application of heat, the yield of oil was found to be 0.1 per cent.

By careful manipulation a yield of 0.95 per cent of volatile oil was obtained from the press cake which remained after the extraction of the fixed oil from the kernels. This is equivalent to nearly 1 pound of oil from every 100 pounds of press cake.

It is recommended that the volatile oil be extracted from the kernels rather than from the pits direct, both from an economical standpoint and from the ease of manipulation, since much loss is avoided in working with the smaller volume of material in the form of the press cake than with the much larger bulk of ground pits.

# PHYSICAL AND CHEMICAL PROPERTIES OF THE VOLATILE OIL.

The physical and chemical properties of the volatile oil were determined and together with the yields were tabulated with other kernel oils, which included several market samples of bitter-almond oil. According to the United States Pharmacopæia, bitter-almond oil is designated as being derived from bitter almonds and "other seeds containing amygdalin." Cherry kernels contain amygdalin, and cherry oil should therefore belong to the same class as bitter-almond oil.

The data obtained from the physical and chemical examination of the volatile oils are presented in Table VII.

An examination of Table VII shows that the yield of cherry oil was somewhat less than that of the other oils. This is explained by the fact that the kernels used in the experiment were from pits which had been in the laboratory for a considerable length of time and had undoubtedly deteriorated. The yield of oil from fresh kernels would very probably be higher. However, the yield obtained was sufficient to justify the use of cherry kernels for the production of oil.

 $<sup>^{1}\,\</sup>mathrm{The}$  Pharmacopæia of the United States . . . Eighth decennial revision, p. 306. Philadelphia, 1907.

Table VII.—Yield, physical properties, and chemical composition of the volatile oils from various fruit sources.

| Source of oil.                                       | Yield<br>from<br>press<br>cake. | Color.              | Odor.  | Taste.                                 | Spe-<br>cific<br>gravity<br>at 24 C. | H Cn.1          | Benzal-<br>de-<br>hyde.² |
|--|---------------------------------|---------------------|--|--|--------------------------------------|-----------------|--------------------------|
| Cherry kernels                                       | Per cent.<br>0.95               | Pale straw          | Pleasant,<br>strong, bit-<br>ter-almond-<br>like.      | Sweet and very pungent.                | 1.050                                | Per ct.<br>4.21 | Per ct. 3 81.53          |
| Cherry pits  | .10                             | Golden yel-<br>low. | Agreeable<br>charac-<br>teristic.                      | Sweet, strong,<br>pungent.             | 1.012                                | 7.94            | 67.95                    |
| Peach kernels 4                                      | 1.17                            | Pale straw          | Bitter-almond-<br>like, some-<br>what irritat-<br>ing. | Sweet and pungent.                     | 1.068                                | 2.20            | 73.1                     |
| Apricot kernels4                                     | 1.33                            | Straw               | Aromatic,<br>almond-like.                              | Sweet and in-<br>tensely pun-<br>gent. | 1.080                                | 2.05            | 3 88.7                   |
| Prune kernels4                                       | .71                             | Faint straw.        | Strong benzal-<br>dehyde.                              | Sweet and pungent.                     | 1.050                                | 1.75            | 76                       |
| Bitter almonds 4                                     | 1.15                            | do                  | Less aromatic<br>(fainter than<br>above).              | Sweet, less<br>pungent.                | 1.056                                | 4.80            | 62                       |
| Bitter-almond oil<br>(market sample 2<br>vears old). |                                 | Golden              | Characteristic,<br>mellow.                             | Very pungent.                          | 1.059                                | 2.57            | 78.45                    |
| Bitter-almond oil<br>(market sample 1<br>year old).  |                                 | Pale yellow.        | Strong and penetrating.                                | Sweetish pun-<br>gent.                 | 1.058                                | 2.12            | 80.6                     |
| Benzaldehyde (sev-<br>eral years old).               |                                 | Deep yel-<br>low.   | do   | Very sweet, pungent.                   | 1.062                                | 513.7           | 77.5                     |

Assayed according to the volumetric method of the Pharmacopæia of the United States, Eighth decennial revision, p. 306. Philadelphia, 1907.
 Assayed by the sodium bisulphite method. The Pharmacopæia. Loc. cit.

8 Assayed immediately after distillation.

<sup>4</sup> Rabak, Frank. Peach, apricot, and prune kernels as by-products of the fruit industry of the United States. U. S. Dept. Agr., Bur. Plant Indus. Bul. 133, p. 23, 25, 1908. 5 Benzoic acid.

The physical properties do not differ greatly; in fact, they nearly coincide with those of the other oils. In hydrocvanic-acid content the cherry oil was found to be somewhat higher than in the other oils, but it was nearly within the limits of the Pharmacopæia, which requires not less than 2 nor more than 4 per cent. The benzaldehyde content, which, because of its instability under ordinary means of preservation fluctuates noticeably in this class of oils, compares favorably with the other kernel oils. The pharmacopæial requirement with regard to benzaldehyde content is that it shall not be less than 85 per cent. benzaldehyde content of the cherry oil, although lower than the requirement, is not as low as in the two samples of bitter-almond oil purchased in the open market, both of which were slightly deficient on account of deterioration, which was undoubtedly due to the age of This deterioration in benzaldehyde content is more or less rapid, because of the ease with which it oxidizes to benzoic acid. The sample of benzaldehyde examined illustrates the change which takes place under ordinary conditions. The sample, which originally was a pure compound, after standing for several years shows but 77.5 per cent of benzaldehyde. The free acidity, calculated as benzonic acid. was 13.7 per cent. The benzaldehyde content bears a direct relationship to the specific gravity; the higher the benzaldehyde content the lower the specific gravity.

On the whole, the properties of cherry oil compare very favorably with the commercial oils, considering the many unfavorable factors which unavoidably enter into the distillation on a laboratory scale, and it may therefore be considered that for all practical purposes this oil is equal to the oil of bitter almonds and the other kernel oils.

# AVAILABLE QUANTITY OF THE VOLATILE OIL.

Approximating the total available quantity of kernels from the domestic cherries at 448 tons and deducting 30 per cent, the quantity of fixed oil capable of being extracted, there would remain about 314 tons of press cake. It has been shown that 0.95 per cent of volatile oil can be obtained from the press cake, and there would result, therefore, practically 3 tons of volatile oil, or 6,000 pounds.

# USES OF THE VOLATILE OIL.

Bitter-almond oil, aside from its use for medicinal purposes, finds a widespread use in the manufacture of perfumery and confectionery. In the perfumery trade the demand is for the genuine oil rather than for the synthetic article, as the odoriferous properties are much finer and more agreeable. The importation of bitter-almond oil for the year ended June 30, 1914, reached a total of 7,525 pounds, valued at \$21,954,¹ showing that the demand for this oil is keen. For some time prior to August, 1914, the price of bitter-almond oil has shown a gradual increase, the wholesale market quotations ranging from \$3.25 to \$4.75 in 1910 ² to \$3.50 to \$6.50 during the first six months of 1914.² Since then the price has risen rapidly, due apparently to lack of importations. At the present time (January, 1916) the oil is quoted at \$9.25 to \$11 a pound.³

#### VALUE OF THE VOLATILE OIL.

Assuming that 6,000 pounds of volatile oil can be produced annually, the gross income from the total available output of kernels, calculated at the minimum price quoted at the present time, would be \$46,500. Therefore it would seem reasonable to suppose that the production of volatile oil from waste cherry pits should meet with favorable attention as a means of converting the now useless waste into a source of profit.

# CHERRY-KERNEL MEAL.

#### CHEMICAL CONSTITUENTS.

After distilling the volatile oil from the press cake, the residue which remained consisted of a mushy mass. The moisture was re-

<sup>&</sup>lt;sup>1</sup>U. S. Department of Commerce. Foreign Commerce and Navigation of the United States for the Year Ending June 30, 1914, p. 821. Washington, 1915.

<sup>&</sup>lt;sup>2</sup> Oil, Paint, and Drug Reporter.

<sup>3</sup> Oil, Paint, and Drug Reporter, v. 89, no. 3, p. 40. 1916.

moved from this mass partly by pressure and partly by drying, after which the dried mass was ground to a meal. Upon examination, the meal was found to contain 1.06 per cent of moisture; 3.94 per cent of ash; 13.1 per cent of ether extract; 30.87 per cent of protein; 8.9 per cent of crude fiber, and 42.13 per cent of nitrogen-free extract.

8.9 per cent of crude fiber, and 42.13 per cent of nitrogen-free extract. In order to interpret these results with regard to the value of the meal as a stock food, in which it probably would find its chief use, comparison of the various constituents was made with those of several feeding stuffs as recorded by Henry. The comparison is shown in Table VIII.

 $\begin{array}{lll} \textbf{Table VIII.--Cherry-kernel meal compared with various commercial feeding} \\ stuffs. \end{array}$ 

|   | Constituents (per cent).                   |  |   |  |  |   |  |  |  |  |
|---|--|--|---|--|--|---|--|--|--|--|
| Feeding stuff.  | Moisture.                                  | Ash.   | Protein.  | Nitrogen-<br>free ex-<br>tract.  | Fiber.   | Ether extract.  |  |  |  |  |
| Cherry, kernel meal   | 1.06                                       | 3.94   | 30.87   | 42.13  | 8.9  | 13.1  |  |  |  |  |
| Soy-bean cake Linseed meal Cottonseed meal Coconut cake Palm-nut cake Sunflower-seed cake. Peanut cake Rape-seed cake. Sesame-oil cake. Corn meal | 9.8<br>7.0<br>10.3<br>10.4<br>10.8<br>10.7 | 5.9<br>5.5<br>6.6<br>5.9<br>4.3<br>6.7<br>4.9<br>7.9<br>8.8<br>1.4 | 42.7<br>33.9<br>45.3<br>19.7<br>16.8<br>32.8<br>47.6<br>31.2<br>36.7<br>9.2 | 28.1<br>35.7<br>24.6<br>38.7<br>35.0<br>27.1<br>23.7<br>30.0<br>17.3<br>68.7 | 6.0<br>7.3<br>6.3<br>14.4<br>24.0<br>13.5<br>5.1<br>11.3<br>3.8<br>1.9 | 6.0<br>7.8<br>10.2<br>11.0<br>9.8<br>9.<br>8.0<br>9.0<br>26.0 |  |  |  |  |

The low percentage of moisture in the cherry-kernel meal is due to the fact that the material was dried just before the determination was made. The percentage of ash is somewhat lower than in any of the other feed cakes, with the exception of corn.

From the standpoint of food value the most important constituents are the ether extract, consisting largely of fat and other soluble constituents; the protein, consisting of nitrogen compounds; and the nitrogen-free extract, which includes soluble carbohydrates, such as sugar, starch, gums, etc. The meal is considerably richer in ether extract than any of the foods enumerated, with the exception of sesame-oil cake. In content of nitrogen-free extract it excels nearly all. The protein content, also, compares very favorably with the more important feeding stuffs of commerce. The percentage here given is doubtless below the actual percentage of soluble carbohydrates, due to the partial extraction of the water-soluble compounds of the meal by the water contained in the still after distillation. To illustrate: It was found that the water extract from the distillation of a quantity of ground pits, after evaporation to dryness, constituted 6.7 per cent of the original ground material. The solid extract after powdering was chocolate brown in color, with a rather pleasant

Henry, W. A. Feeds and Feeding . . . ed. 10, p. 566-567. Madison, Wis., 1910.

taste suggesting roasted grain. This extract was readily soluble in water. The protein content was found to be 33.93 per cent. The utilization of this waste water-soluble extract by evaporation with the meal left in the still would add much to the nourishing properties of the meal. The fiber content, although not high in comparison with some of the other meals, was augmented by the presence in the kernels, before grinding, of particles of the pits which escaped separation in the cracking process.

AVAILABLE QUANTITY, USES, AND VALUE OF CHERRY-KERNEL MEAL.

Roughly estimated, the total available quantity of meal which would result after extracting the oil would be about 300 tons from the domestic cherries and 30 tons from the imported cherries.

The utility of the meal, as shown by its composition, should be similar to that of the general class of oil cakes now sold on the market for stock foods.

Regarding the commercial value only an estimate can be made. Based on the current prices of linseed meal, which is about \$39 per ton, the estimated money value of the yearly output of cherry-kernel meal would be about \$12,870.

# COMMERCIAL PRODUCTS OBTAINABLE FROM CHERRY JUICE.

Attention has already been called to the large quantity of juice which accumulates during the operation of pitting cherries. The juice is bright red in color, with the odor and taste of cherries. Using the sugar and acid content as a basis for investigation, several experiments were conducted, with a view to preparing products which might be of commercial value.

#### ALCOHOL FROM CHERRY JUICE.

In order to convert the cherry juice into alcohol, a cake of compressed yeast was added to 1 kilo of filtered juice and the mixture kept at 30° C. for a period of 24 hours, with occasional agitation. After this period, fermentation had completely ceased. The mixture was then filtered, neutralized with milk of lime, and distilled. A small quantity of phosphoric acid was added to the distillate and a second distillation made. The alcohol obtained was deodorized by the addition of potassium permanganate and again distilled. By this method it was calculated that 4.36 per cent of absolute alcohol, or 4.6 U. S. P. alcohol (95 per cent by volume), could be prepared from the waste juice.

# SIRUP FROM CHERRY JUICE.

For the preparation of sirup, a quantity of the filtered juice was evaporated in vacuo after previously neutralizing the acidity with milk of lime. The calcium salts of the acids were filtered from the hot sirup by means of vacuum filtration. This procedure was carried on twice during the concentration of the juice. The yield of sirup obtained was about 20 per cent. The calcium salts (probably consisting largely of calcium malate) after drying resulted to the extent of 1.35 per cent. The sirup obtained was dark brown in color, with a pleasant, sweet, slightly tart taste.

The specific gravity at 24° C. was 1.34. Assayed gravimetrically by means of Fehling's solution the content of reducing sugars was found

to be 43 per cent and the total sugars 52.1 per cent.

The free acidity was determined by titration with N/10 potassium hydroxid V. S. and calculated as malic acid by means of the malicacid factor (1 c. c. N/10 KOH=0.0067 gm. malic acid). The sirup was found to contain 1.3 per cent of malic acid.

These properties of the sirup are most variable and are subject to fluctuation, depending to a great extent upon the consistency to which the sirup is evaporated. The greater the concentration the higher the percentage of the important constituents.

#### JELLY FROM CHERRY JUICE

For the preparation of jelly the cherry juice was concentrated with cane sugar (1 pound of sugar to 1,200 c. c. of juice) in a vacuum to a sirupy consistency. Purified gelatin was then added (one-half ounce of gelatin dissolved in one-half pint of water) and the mixture set aside in a cool place. The resulting jelly was wine red in color, with a fruity odor and a very pleasant tart taste.

Although this process is a very crude one, it shows the possibility of converting the juice into a product which is decidedly wholesome. Other processes of preparing jelly from juices of this nature by the use of pectin or parings from fruits which are rich in pectin would doubtless be productive of even more promising results.

Calculated with the amount of sugar added it was found that about

81.6 per cent of jelly could be prepared from the juice.

AVAILABLE QUANTITY, USES, AND VALUE OF THE ALCOHOL, SIRUP, AND JELLY FROM CHERRY JUICE.

The prospect of profitably converting the juice into commercially useful products would depend largely upon the available quantity. As previously stated, approximately 105,000 gallons of juice result from the pitting process. The alcohol production from this quantity of juice would be about 5,000 gallons. The usefulness and commercial value of alcohol is well known and needs no further comment.

The quantity of sirup capable of being manufactured from the total available juice, calculating the yield of sirup as 20 per cent, would be 21,000 gallons. The usefulness of the sirup as a household commodity can hardly be questioned. It is also possible that it could

be reapplied to the canning of cherries, much as the sirup from pineapple waste is at present utilized. The value must necessarily be determinated by the uses to which it can be put and the demand created thereby. Its pleasant taste and agreeable flavor should create a demand for the product as a table commodity.

The total quantity of jelly which could be manufactured from the juice available annually would approximate 85,680 gallons. The actual value of this quantity of jelly can not be accurately estimated, but it can safely be assumed that a considerable margin of profit would result after deducting the expense of manufacture.

# SUMMARY.

To briefly recapitulate the results of the foregoing investigation, it is shown that the waste products from the cherry industry can be reduced to a number of valuable products:

- (1) The fixed oil, which is perhaps the most important product, is, in its properties and general characteristics, so closely related to the commercial oil of almonds that it is placed in an important position with respect to usefulness and value. The oil expressed from the fresh kernels is quite similar to almond oil and its use as an article of commerce, applied along pharmaceutical and therapeutical lines, or as a condimental oil, or even for soap-making purposes, should be assured.
- (2) The volatile oil which can be produced from the press cake after the fixed oil has been extracted is practically identical with the oil of bitter almonds, thus rendering its usefulness the same in every way as that of bitter-almond oil.
- (3) The meal, which is the final residue, has been shown to possess nourishing properties, much the same as those of the more common feeding stuffs on the market.
- (4) The juice has been shown to be capable of being transformed into alcohol, sirup, or jelly, and it is reasonable to assume that there should be a demand for such products.

The success of an undertaking involving the by-products in question would depend largely upon the efficacy of any proposed system whereby the products could be manufactured. Since the waste as it accumulates is not confined to any particular section, perhaps the most feasible method would be to accumulate the waste at some central point. The most convenient plan then would be to conduct the manufacture on a cooperative basis, much as the present system of cooperative creameries is conducted, whereby the cream produced in any dairy section is conducted to a central plant where the products are manufactured.

While the object of this investigation is principally to point out the possibilities existing in the cherry by-products, it is hoped that the information contained herein will serve as an incentive to the proper disposition of these waste products, with their ultimate reduction into products of commercial utility and value.